Structure-property correlations in piracetam polytypes

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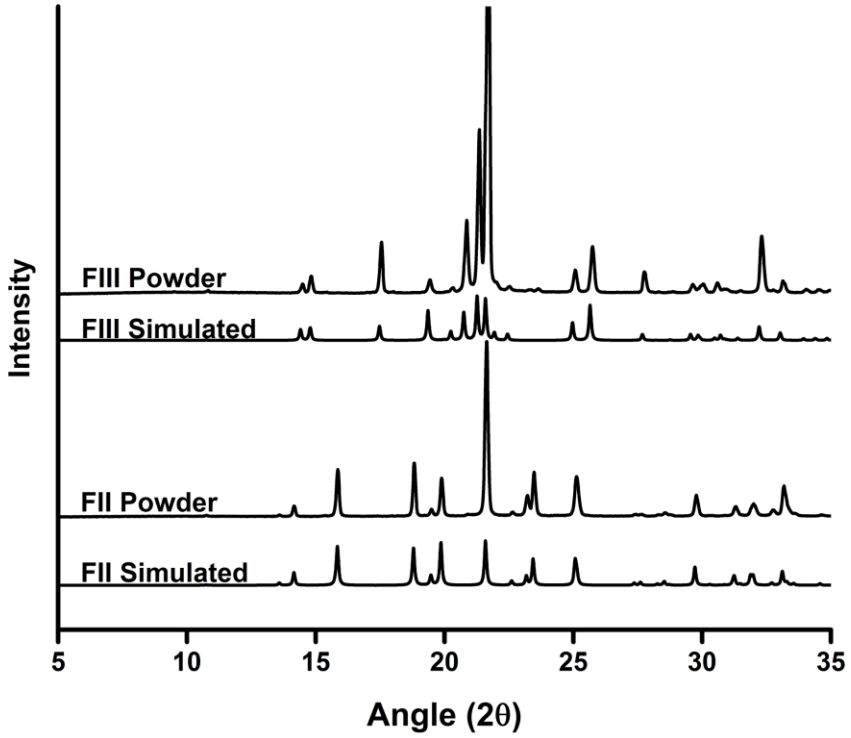
S1. Comparison of experimental and simulated PXRD patterns for piracetam bulk phases



S2. PIXEL calculations: FII (CSD: BISMEV11, space group *P*–1, transformed using the matrix [1 0 0, 0 –1 0, 0 0 –1])

Unit cell: a = 6.353, b = 6.528, c = 8.372 Å, alpha = 80.30, beta = 101.77, gamma = 90.95°
Symmetry operators: [1] x, y, z [2] –x, –y, –z

Shaded rows indicate interactions between polytypic layers. Only interactions with magnitude > 3 kJ mol^{-1} are listed.

Mol 1 ARU	Mol 2 ARU	Mol 1 Operator	Mol 2 Operator	Distance	Coulomb	Polarisation	Dispersion	Repulsion	Total
1_555_01	2_456_01	x,y,z	-1-x,-y,1-z	7.856	-98.5	-34.0	-20.0	90.4	-62.2
1_555_01	1_655_01	x,y,z	1+x,y,z	6.353	-47.5	-16.4	-21.3	43.5	-41.6
1_555_01	1_455_01	x,y,z	-1+x,y,z	6.353	-47.5	-16.4	-21.3	43.5	-41.6
1_555_01	2_567_01	x,y,z	-x,1-y,2-z	4.698	-16.7	-7.5	-34.5	28.9	-29.8
1_555_01	2_557_01	x,y,z	-x,-y,2-z	6.288	-28.0	-9.8	-12.2	21.0	-29.1
1_555_01	2_566_01	x,y,z	-x,1-y,1-z	5.120	-17.6	-7.7	-21.1	19.0	-27.4
1_555_01	2_466_01	x,y,z	-1-x,1-y,1-z	5.216	-4.6	-2.8	-18.3	9.6	-16.1
1_555_01	1_545_01	x,y,z	x,-1+y,z	6.528	-4.4	-3.6	-14.5	11.6	-10.9
1_555_01	1_565_01	x,y,z	x,1+y,z	6.528	-4.4	-3.6	-14.5	11.6	-10.9
1_555_01	2_457_01	x,y,z	-1-x,-y,2-z	7.801	-2.2	-1.6	-5.0	0.7	-8.2
1_555_01	2_667_01	x,y,z	1-x,1-y,2-z	8.949	-3.7	-0.5	-1.5	0.0	-5.7
1_555_01	1_645_01	x,y,z	1+x,-1+y,z	9.184	-3.0	-0.2	-0.3	0.0	-3.5
1_555_01	1_465_01	x,y,z	-1+x,1+y,z	9.184	-3.0	-0.2	-0.3	0.0	-3.5
1_555_01	2_556_01	x,y,z	-x,-y,1-z	7.880	8.8	-0.6	-0.9	0.0	+7.3
1_555_01	2_657_01	x,y,z	1-x,-y,2-z	9.947	8.6	-0.4	-0.3	0.0	+8.0

S2. PIXEL calculations: FIII (CSD: BISMEV12, space group $P2_1/n$)

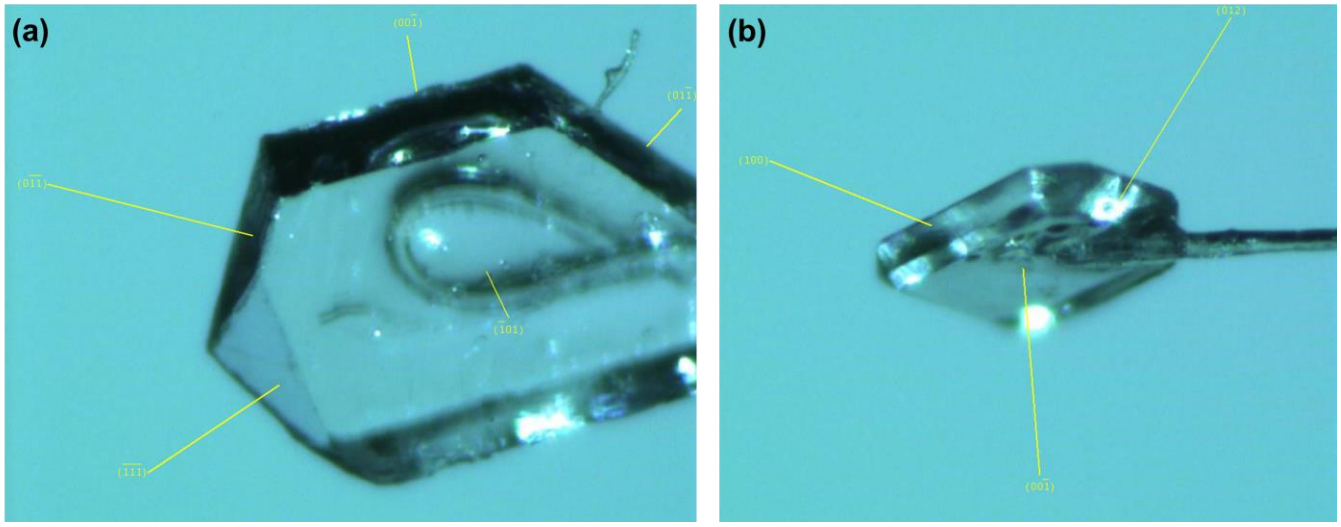
Unit cell: a = 6.454, b = 6.386, c = 16.181 Å, alpha = 90, beta = 92.06, gamma = 90°
Symmetry operators: [1] x, y, z [2] 0.5-x,0.5+y,0.5-z [3] –x, –y, –z [4] 0.5+x,0.5-y,0.5+z

Shaded rows indicate interactions between polytypic layers. Only interactions with magnitude > 3 kJ mol^{-1} are listed.

Mol 1 ARU	Mol 2 ARU	Mol 1 Operator	Mol 2 Operator	Distance	Coulomb	Polarisation	Dispersion	Repulsion	Total
1_555_01	3_565_01	x,y,z	-x,1-y,-z	7.851	-101.9	-35.7	-20.4	92.3	-65.8
1_555_01	1_655_01	x,y,z	1+x,y,z	6.454	-47.5	-17.1	-21.5	44.8	-41.3
1_555_01	1_455_01	x,y,z	-1+x,y,z	6.454	-47.5	-17.1	-21.5	44.8	-41.3
1_555_01	3_655_01	x,y,z	1-x,-y,-z	5.124	-18.3	-8.2	-21.1	19.5	-28.1
1_555_01	2_545_01	x,y,z	0.5-x,-0.5+y,0.5-z	5.176	-17.5	-6.3	-22.4	19.3	-27.0
1_555_01	2_555_01	x,y,z	0.5-x,0.5+y,0.5-z	5.176	-17.5	-6.3	-22.4	19.3	-27.0
1_555_01	3_555_01	x,y,z	-x,-y,-z	5.258	-5.9	-3.0	-18.9	11.1	-16.7
1_555_01	1_545_01	x,y,z	x,-1+y,z	6.386	-6.2	-4.4	-15.9	14.6	-11.9
1_555_01	1_565_01	x,y,z	x,1+y,z	6.386	-6.2	-4.4	-15.9	14.6	-11.9
1_555_01	1_445_01	x,y,z	-1+x,-1+y,z	9.079	-3.1	-0.2	-0.3	0.0	-3.7
1_555_01	1_665_01	x,y,z	1+x,1+y,z	9.079	-3.1	-0.2	-0.3	0.0	-3.7
1_555_01	3_665_01	x,y,z	1-x,1-y,-z	7.762	9.6	-0.7	-0.9	0.0	+8.0

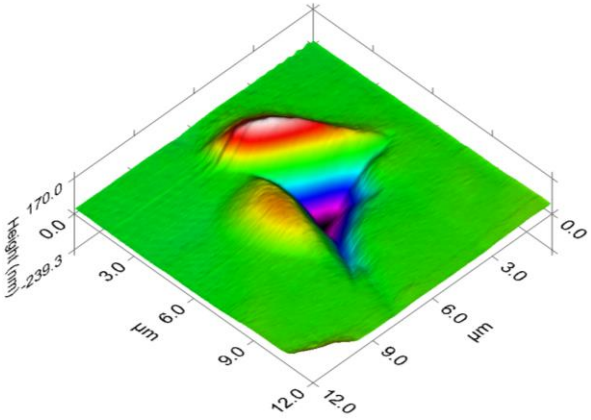
S3. Face identification of single crystals

Major faces for indentation were identified by morphology analysis on the single-crystal X-ray diffractometer (*APEX3* software package, Bruker AXS). SEM images were collected to correlate the identified faces with the crystal morphology in bulk samples. Crystals of FIII display a plate-like morphology, so only the major face {001} is available for nanoindentation. Crystals of FII have a more block-like shape, and both {001} and {10–1} faces are available for nanoindentation.

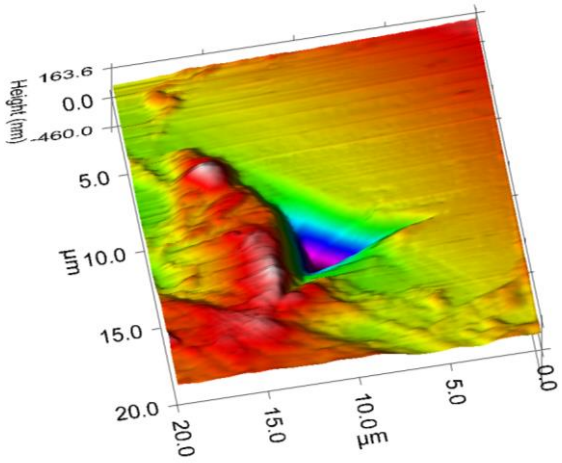


Face indexed crystals: (a) {001} and {10–1} face of FII; (b) {001} face of FIII

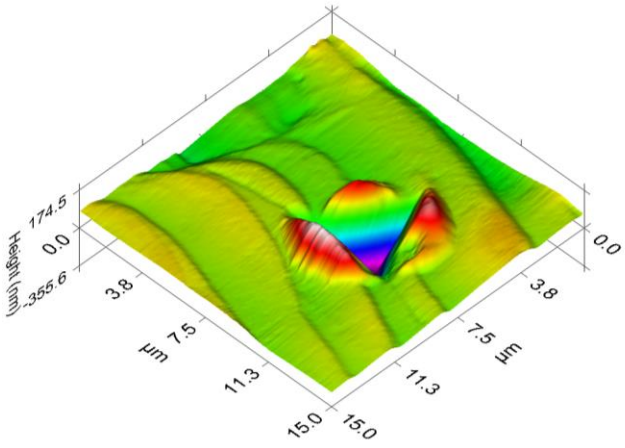
S5. AFM images following nanoindentation



FII {001}



FII {10–1}



FIII {001}

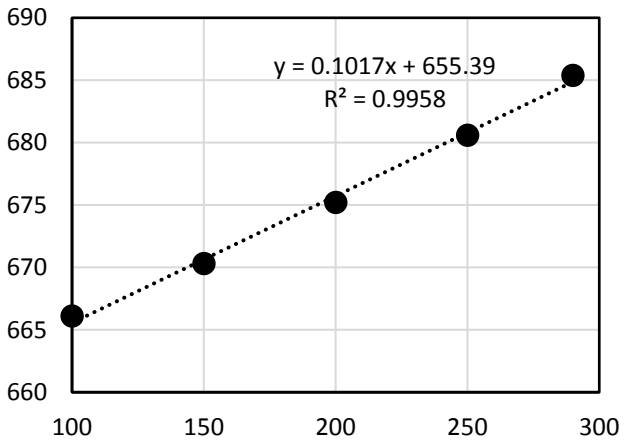
S6. Thermal expansion measurements

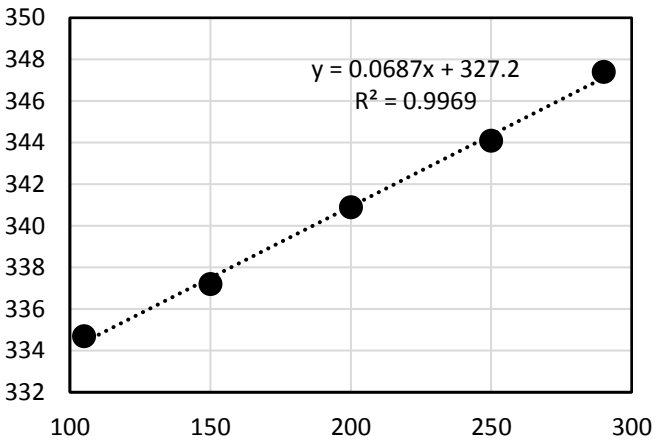
Unit-cell parameters (Å, °) were measured over the range *ca* 100–300 K at for single crystals.

FII	T (K)	a	b	c	α	β	γ	Volume
	105	6.357	6.515	8.377	80.23	101.76	90.99	334.7
	150	6.363	6.541	8.402	80.24	100.90	90.97	337.2
	200	6.372	6.572	8.449	80.12	102.01	90.99	340.9
	250	6.390	6.598	8.496	79.94	102.17	91.11	344.1
	290	6.402	6.609	8.542	79.89	102.39	91.04	347.4

FIII	T (K)	a	b	c	α	β	γ	Volume
	100	6.455	6.383	16.176	90	92.04	90	666.1
	150	6.471	6.387	16.227	90	91.99	90	670.3
	200	6.485	6.398	16.284	90	92.04	90	675.2
	250	6.499	6.408	16.355	90	92.05	90	680.6
	300	6.509	6.419	16.416	90	92.08	90	685.4

Plots of V vs T show a good approximation to linear behavior:



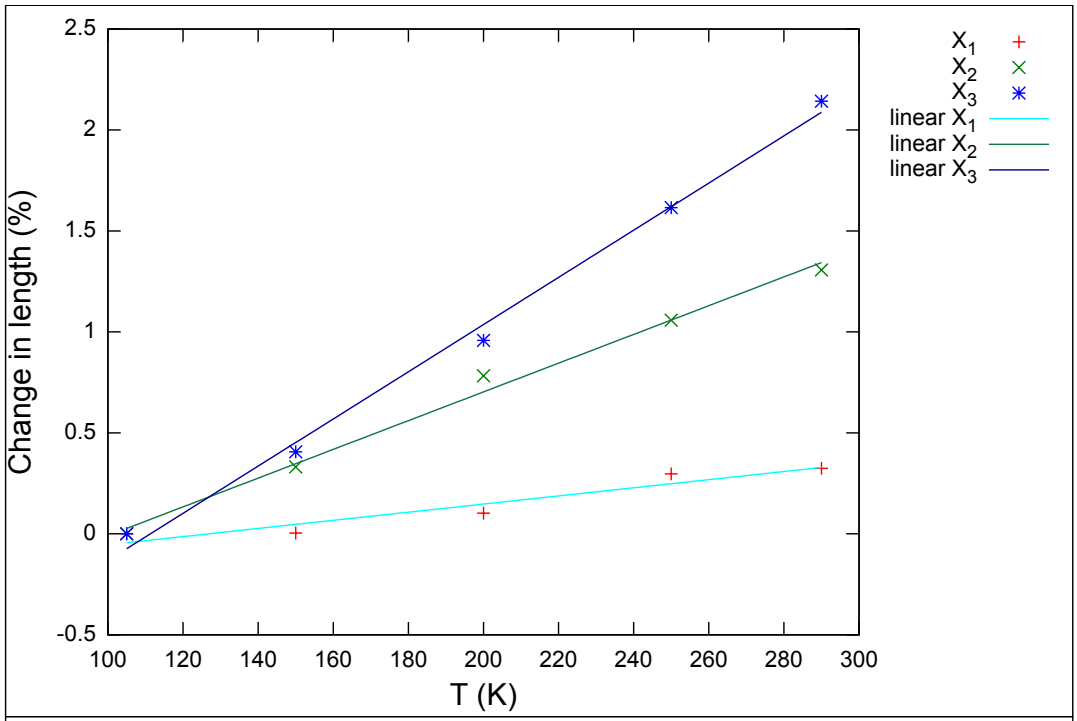


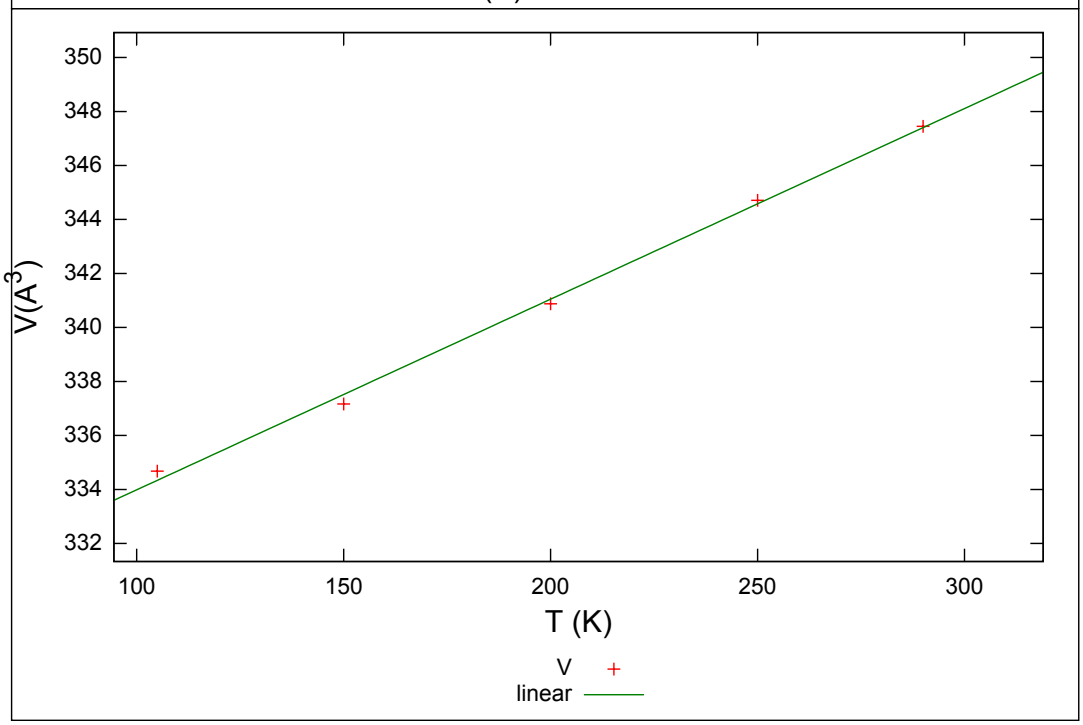
The thermal expansion tensor, principal expansion coefficients and the directions of the principal axes were obtained using the PASCal web tool at the University of Oxford (http://pascal.chem.ox.ac.uk/). The core output from PASCal is appended on the following pages.

Output

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	20.1426	2.3792	0.9430	-0.1088	0.3144
X_2	71.1693	1.9258	0.2231	0.8126	-0.5383
X_3	116.8383	3.9956	0.1424	-0.7665	-0.6262
V	211.0011	4.9554			

Plots





% change in length

T	X_1	X_2	X_3	$X_{1,calc}$	$X_{2,calc}$	$X_{3,calc}$
105.0000	0.0000	0.0000	0.0000	-0.0438	0.0269	-0.0737
150.0000	0.0041	0.3317	0.4065	0.0469	0.3471	0.4521
200.0000	0.1025	0.7824	0.9578	0.1476	0.7030	1.0363
250.0000	0.2971	1.0585	1.6158	0.2483	1.0588	1.6205
290.0000	0.3242	1.3067	2.1429	0.3289	1.3435	2.0878

Volume

T	V (Å^3)	V_{lin} (Å^3)
105.0000	334.6783	334.3387
150.0000	337.1677	337.5165
200.0000	340.8775	341.0474
250.0000	344.7115	344.5782
290.0000	347.4487	347.4029

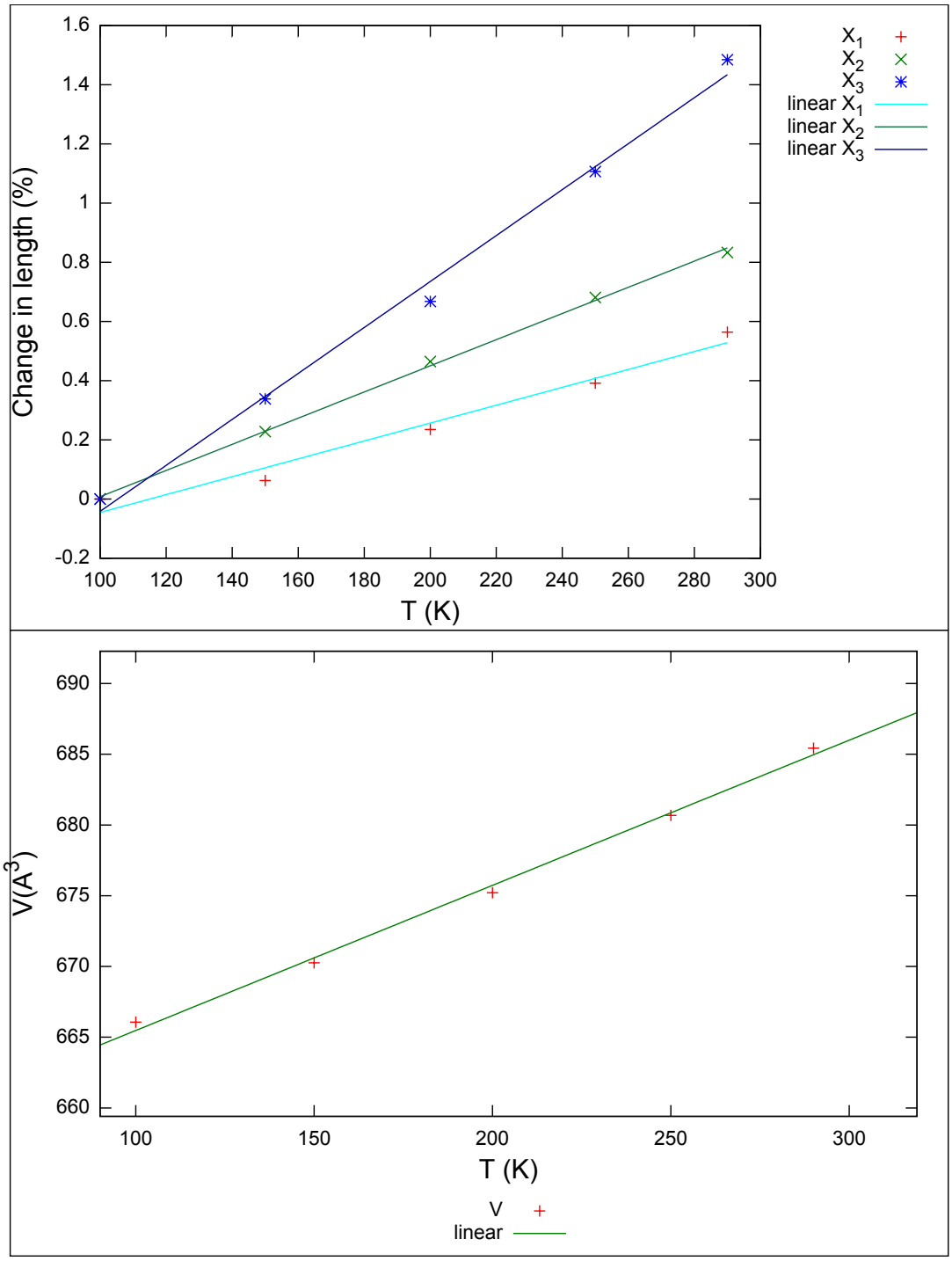
Input

T	σT	a	b	c	α	β	γ
105	5	6.357	6.515	8.377	80.23	101.76	90.99
150	5	6.363	6.541	8.402	80.24	101.90	90.97
200	5	6.372	6.572	8.449	80.12	102.01	90.99
250	5	6.390	6.598	8.496	79.94	102.17	91.11
290	5	6.402	6.609	8.542	79.89	102.39	91.04

Output

Axes	α(MK^{-1})	σα (MK^{-1})	Direction a	b	c
X_1	30.2064	2.5760	-0.0000	1.0000	-0.0000
X_2	44.2187	0.7220	-1.0000	0.0000	-0.0071
X_3	77.6486	2.7147	0.0447	-0.0000	0.9990
V	154.0260	4.7771			

Plots



% change in length

T	X_1	X_2	X_3	$X_{1,calc}$	$X_{2,calc}$	$X_{3,calc}$
100.0000	0.0000	0.0000	0.0000	-0.0454	0.0080	-0.0415
150.0000	0.0627	0.2278	0.3384	0.1057	0.2291	0.3467
200.0000	0.2350	0.4647	0.6677	0.2567	0.4502	0.7350
250.0000	0.3917	0.6810	1.1066	0.4077	0.6713	1.1232
290.0000	0.5640	0.8332	1.4845	0.5286	0.8482	1.4338

Volume

T	V (Å^3)	V_{lin} (Å^3)
100.0000	666.0654	665.4753
150.0000	670.2619	670.6049
200.0000	675.2117	675.7344
250.0000	680.6777	680.8640
290.0000	685.4294	684.9677

Input

T	σT	a	b	c	α	β	γ
100	5	6.455	6.383	16.176	90	92.04	90
150	5	6.471	6.387	16.227	90	91.99	90
200	5	6.485	6.398	16.284	90	92.04	90
250	5	6.499	6.408	16.355	90	92.05	90
290	5	6.509	6.419	16.416	90	92.08	90